



Engineered Nano-bio Hybrid Electronic Platform for Solar Energy Harvesting

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14. ABSTRACT Bacteriorhodopsin is an optoelectric protein found in the membrane of the extremophile bacterium <i>Halobacterium salinarum</i> . The protein creates a charge gradient across its 6 nm thickness and, when integrated with inorganic electron generation and transport materials such as titania nanotubes, may find use in a new class of photon harvesters. Bacteriorhodopsin strongly absorbs light near the 570 nm wavelength but its photoelectric activity is now shown to increase by at least 35% when integrated with ultraviolet (UV)-scavenging quantum dots.					
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1. Objective

The Future Force (FF) Soldier will be equipped with a wide-array of new technologies, essentially all requiring electrical power for operation. It will be critical to incorporate energy harvesting systems into the Soldier's gear to accommodate the power demands and lessen the dependence on cumbersome batteries. Photovoltaic (PV) technology is one such option, but is currently impractical due to high cost, low efficiency, and implementation barriers. The evolutionary development of biological systems, such as the optical protein Bacteriorhodopsin (bR), has created natural and sustainable nanoscale materials with capabilities beyond that of current technology, including a wider absorbance spectrum. Integrating this biological material with inorganics, including semiconductor quantum dots (QDs) and titanium dioxide nanotubes, opens new possibilities for protein sensitized solar cells (PSSC). The objective of this research is to better understand the mechanism of efficient photocurrent generation in the PSSC nanomaterial system for PV.

2. Approach

Bacteriorhodopsin is an optoelectric protein found in the membrane of the extremophile bacterium *Halobacterium salinarum*. The protein creates a charge gradient across its 6 nm thickness and, when integrated with inorganic electron generation and transport materials such as titania nanotubes, may find use in a new class of photon harvesters. Structurally similar to the visual rhodopsin found in the mammalian eye, bR has a wide spectral absorbance and most strongly absorbs visible light in the 570-nm spectral region, as shown in figure 1(a). With the absorbed photonic energy, the protein's retinal undergoes an isomerization and initiates proton pumping across the 5.5-nm-thick protein. Studies have demonstrated that bR can create a constant current output upon illumination, as shown in figure 1(b).

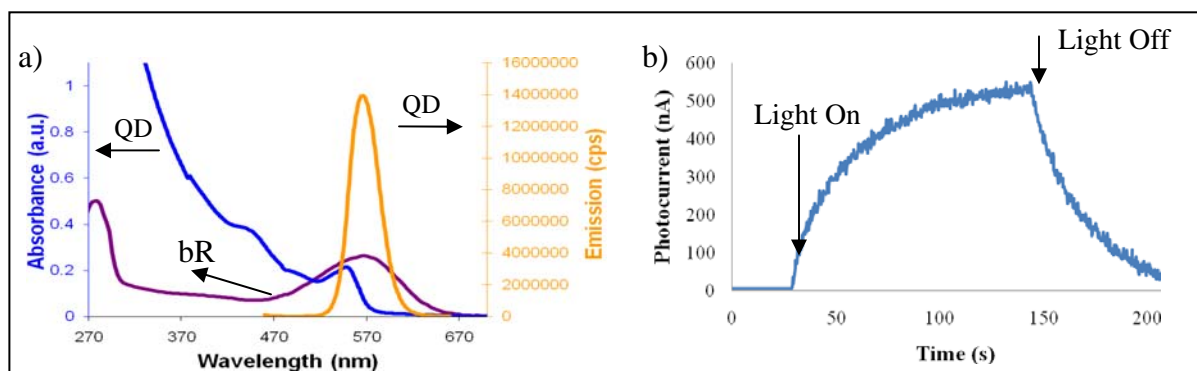


Figure 1. (a) QD absorbance (blue) and emission (orange) properties of QDs and absorbance (purple) of bR; (b) photocurrent generated from 6 oriented monolayers of bR.

Studies show (figure 1a) that the addition of QDs into the bR photovoltaic system greatly extends its absorptive capabilities into the ultraviolet (UV) and shorter wavelength visible range. The QDs can be engineered to re-emit the absorbed light at the wavelength that is most efficiently absorbed by bR, thus increasing the amount of solar energy harvested. In mammalian rhodopsin, the photon bleached retinal (a vitamin A derivative) is expelled from the protein requiring a supply of fresh retinal from the host. bR does not expel the retinal, but instead catalyzes it back to the unbleached form making it a more adaptable photomaterial.

Tests conducted by Griep, et al. (1, 2) showed an increase in the photoelectric response of bR due to photon scavenging of bound semiconductor quantum dots. Figure 2a shows the increase in fluorescence between just bR and bR with attached QDs to confirm the linkage. Figure 2b shows an approximately 35% increase in the bR/QD photovoltage over that of just bR. This confirms that QDs play an important role in enhancing the electrical output of the bR in a photon scavenging system. With this evidence, the current work has focused on integrating bR with 1-D nanostructures, a necessary next step in understanding the contributions of incremental advances in a bio-nano-hybrid photon harvester.

The bR PSSC has an advantage over a dye-sensitized solar cell (DSSC) in the way in which charge is moved. bR is most often used in the form of native cell membrane patches containing many bR monomers. The membrane patches (termed purple membrane [PM]) have a charge differential across the sides of the membrane at neutral pH. Thus, the PM can be oriented and deposited in an electric field, which results in the charge being directed vectorally into the underlying substrate. However, because the bR pumps a proton, this fact may have applicability in helping maintain an adequate supply of “holes” at the bR/electrolyte interface to inhibit exciton recombination. Additionally, the bR pumps a proton (hole) each 10 ms and replaces that proton from the aqueous electrolyte, freeing an electron. This is a directed chemical process, so the probability of the electron-proton recombination may be reduced.

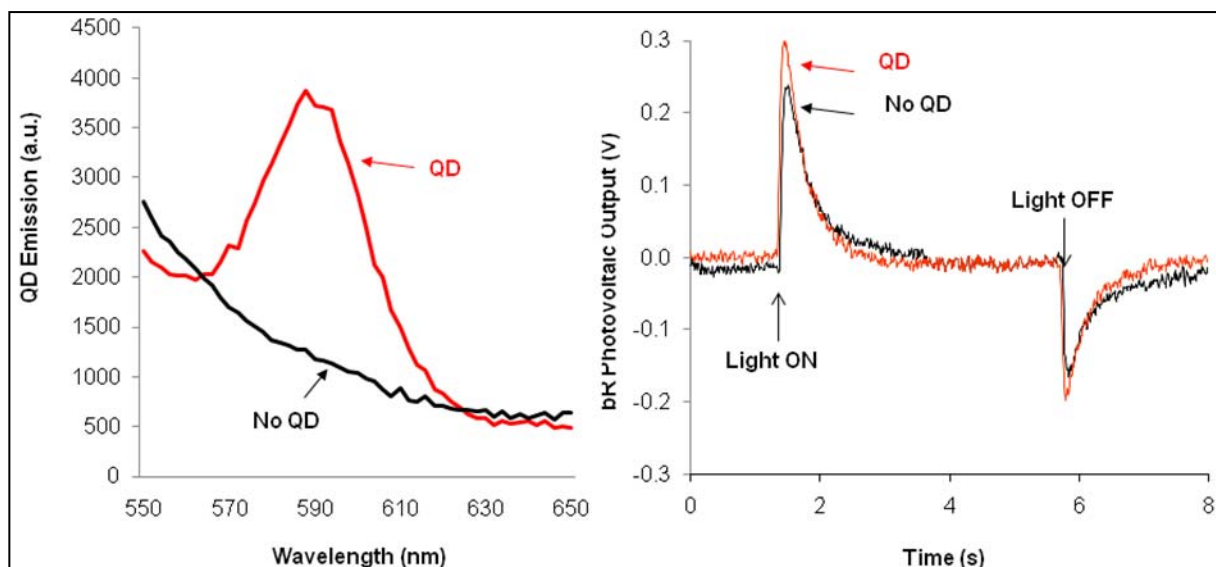


Figure 2. Attachment of quantum dots to bR is confirmed by the large increase of fluorescence upon UV illumination (left). The QD fluorescence and resonance energy transfer to the bR increases the photovoltage by approximately 35% (right).

Coupling bR with QDs as a hybrid greatly increases the optical absorbance. Figure 3 shows the relative bR and QD absorbance, noting that the QD scale is 100 times that of the bR. This means that when integrated over 270–670 nm of optical wavelength, the QDs have an absorbance more than 200 times greater than bR alone. The bR PSSC has an advantage over a DSSC in the way in which charge is moved. bR is most often used in the form of native cell membrane patches containing many bR monomers. The membrane patches (PM) have a charge differential across the sides of the membrane at neutral pH. Thus, the PM can be oriented and deposited in an electric field which results in the charge being directed vectorally into the underlying substrate. However, because the bR pumps a proton, this fact may have applicability in helping maintain an adequate supply of “holes” at the bR/electrolyte interface to inhibit exciton recombination. Additionally, the bR pumps a proton (hole) each 10 ms and replaces that proton from the aqueous electrolyte, freeing an electron. This is a directed chemical process so the probability of the electron-proton recombination may be reduced.

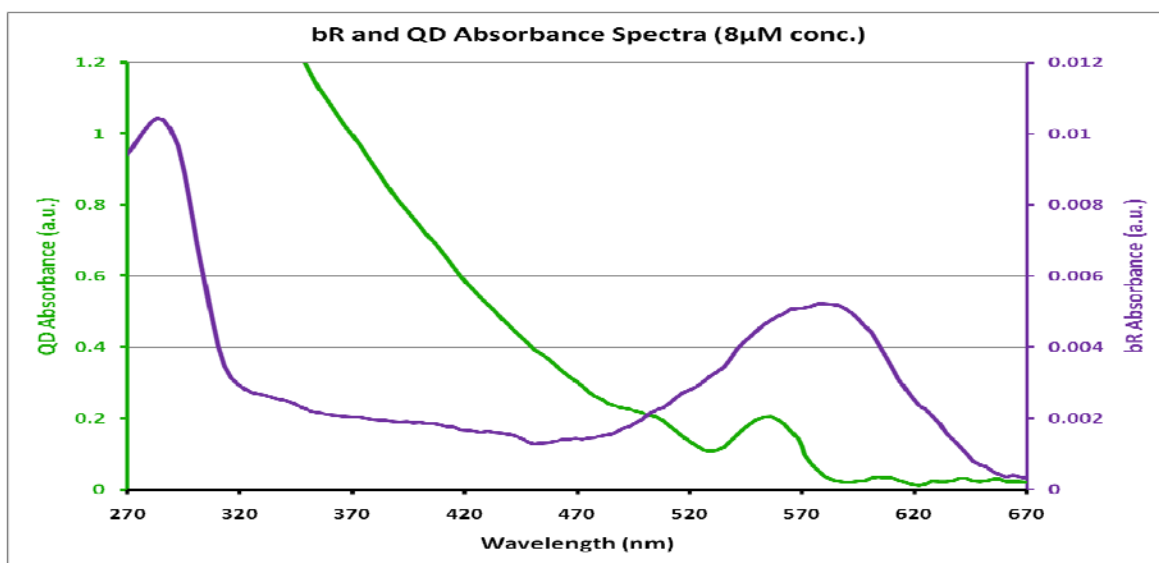


Figure 3. Relative absorbance of bR and QDs, noting the differential scales for each.

To expand research using bR, the cost and time to purify the material must be reduced to make it more accessible. One approach was to identify key cost barriers beyond just volume scale-up, and methods to overcome them. Each chemical component of the growth and purification process steps was quantified and recycling and reuse of the materials was quantified. In addition, bacteria were grown in the recycled materials to validate efficacy.

We conducted experiments to expand the methods developed to increase electrical output of the bR. Quantum dots provide one method, however, this approach does have cost and biochemical processing involved, particularly if the QDs and bR are deposited in highly ordered films by ionic self assembly or Langmuir Blodgett techniques. bR pumps a proton across the membrane, and the bR can support a proton gradient of 10,000:1 (pH of 4 or greater). If the pH on the side of the membrane toward which the protons are pumped is buffered to a higher pH than the endoplasmic side, there should be a greater tendency for proton transfer across the membrane.

3. Results

The bR growth protocols used are both repetitive and yield high purity material as shown by the sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) gels. Strains other than the S9P are available and the R1 strain is considered a very high “over-producer” of the bR protein. In an effort to produce more bR per purified batch and to reduce cost, the R1 strain was cultured using hydrolyzed casein as the nutrition source in place of bacteriological peptone, which is 5-times more expensive. The batches were grown in sealed containers with sufficient headspace to keep the growth aerobic. The rate of bacterial growth greatly increased, which was expected, but only red membrane formed which is void of bR. When the headspace was

reduced, forcing anaerobic growth conditions, the resulting cell pellets were dark purple apparently indicating significant bR content. However, after purification analysis showed a void of bR possibly indicating that the casein nutrient will not suffice for this bacteria or R1 strain.

In an effort to reduce the growth time of the original bacteria, the optical density (OD) of the growth medium was measured at 600 nm as a function of growth time. The cells absorb strongly at 600 nm. The data is shown in figure 4. There are many readings at each of many times from 85 to 265 h of growth. The OD ranges from approximately 0.5 at 85 h of growth to approximately 1.0 at 265 h of growth. The increase in OD indicates an approximate three-fold optical absorbance, assuming an approximate three-fold concentration in cells. The time is also approximately three-fold indicating a linear growth phase. Under these conditions, and because of reactor downtime during medium change out and subsequent inoculation, it is more cost effective to grow the bacteria in larger volumes.

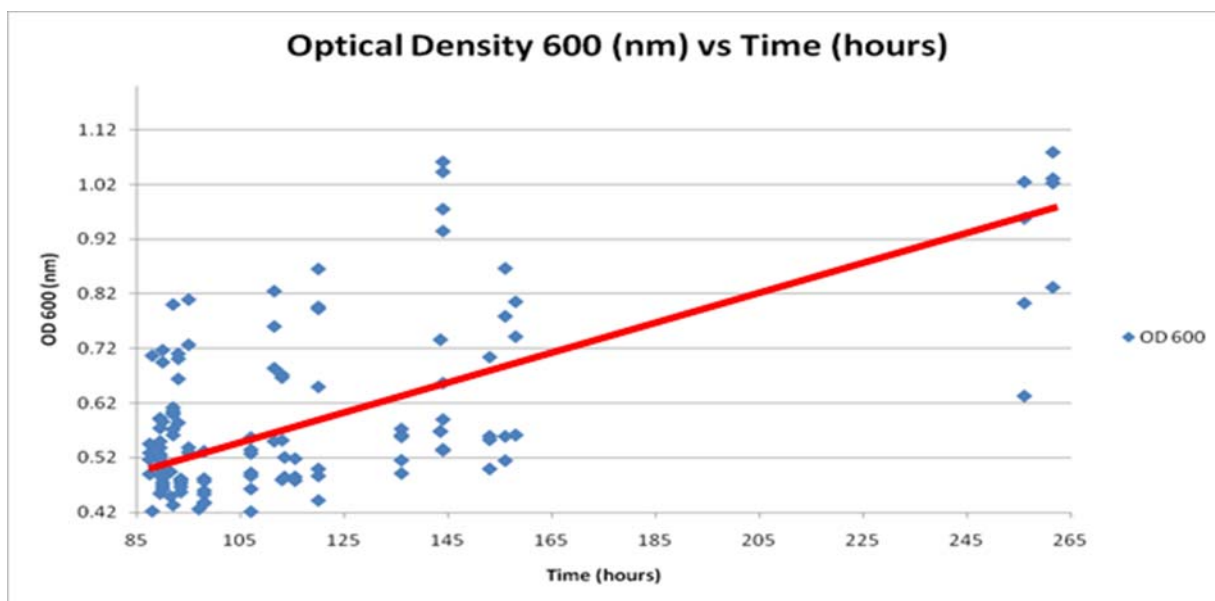


Figure 4. Optical density indicating bacterium growth over time. The trend of the data is approximately linear indicating stable growth.

During operation of a bR bio-solar cell, data suggests that buffering the electrolyte to a basic pH may increase the performance, as shown in figure 5. In this case the potassium chloride (KCl) electrolyte was buffered to produce random (not monotonic) pH values greater than 5.6 which is the isoelectric point of bR. The result shows that up to approximately 7 pH there is only a slight increase in voltage produced by the bR, but at higher pH the voltage increases quite rapidly. This finding would support the hypothesis that an electrolyte with a higher pH could increase solar cell performance.

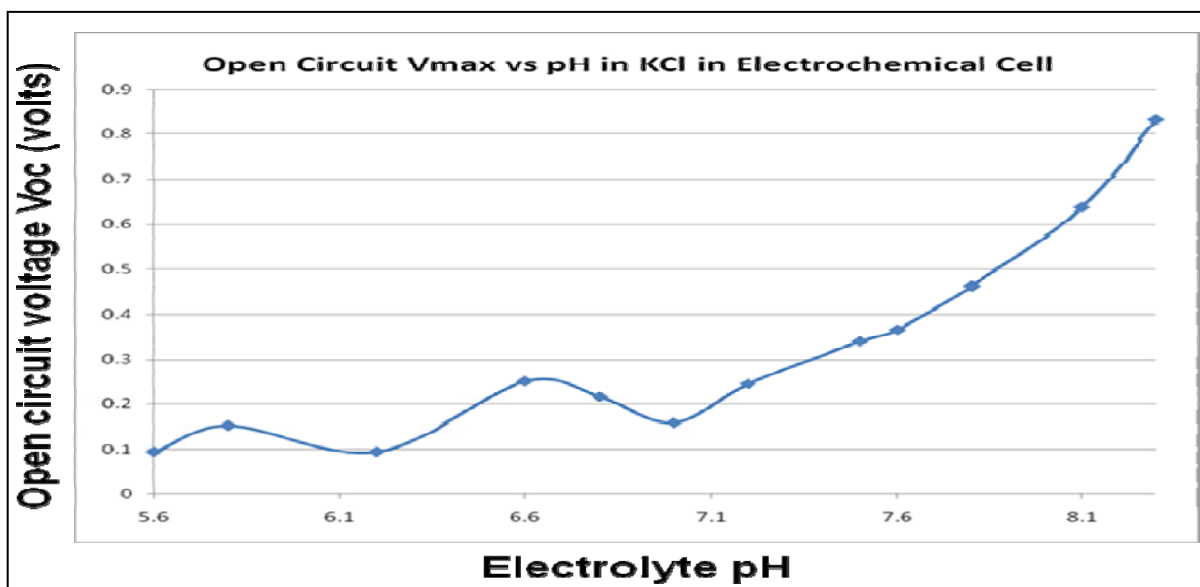


Figure 5. bR open circuit voltage in a KCl electrochemical cell showing a greater voltage response at a higher pH.

We know that under prolonged intense light the bR photobleaches, reducing the absorbance. However, the output photovoltage of oriented bR under prolonged exposure had not been quantified. We conducted long term tests to investigate this reduction. Figure 6 is a typical response. During the first 3 min, the bR was in darkness. Approximately 1-sun was applied whereby the voltage rose from 0.7 to 1.0 V. From then on, the voltage slowly decayed at a rate of approximately 0.4% per minute.

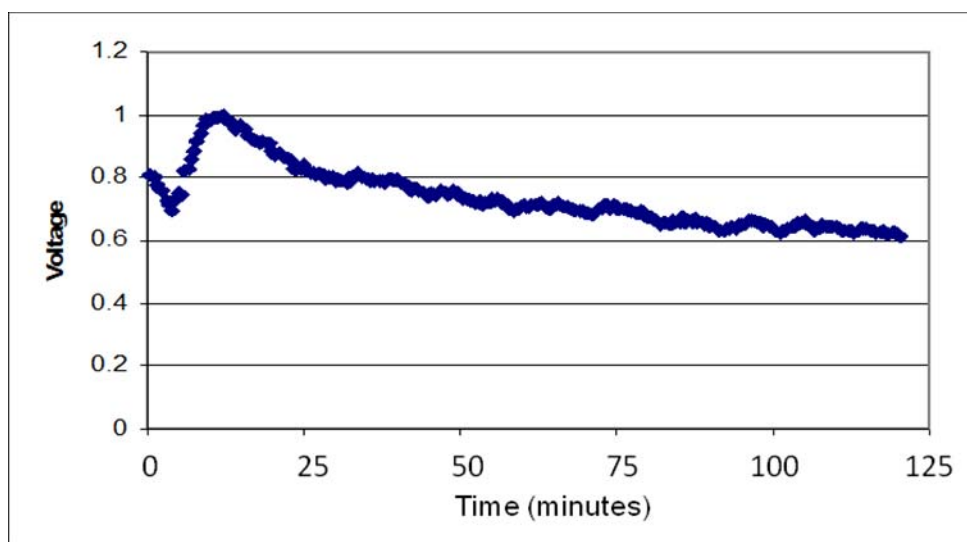


Figure 6. Approximately 2-h time response of bR photovoltage showing slow decay.

4. Conclusions

Second year work has shown that the photovoltage output of bR is enhanced with the integration of semiconductor quantum dots attached with the biotin-streptavidin linkage. This represents the first incremental improvement in increasing photon-to-electrical transduction in the bio-nano hybrid. Building upon this, it has been shown that the photovoltage can also be increased across oriented purple membrane patches by raising the cytoplasmic side of the membrane to a pH above approximately 7.2. At a pH between 7.2 and 8.2, the photovoltage increased by nearly threefold. Several investigations also looked at methods to increase bR production rate. One method was to switch to a different bacterial strain, but those results were inconclusive. Another method was to investigate the development of a real-time cell density measurement scheme. We concluded that it will be better to grow the bacteria in a single large reactor rather than in a reactor one-nth the size and that harvesting the cells n-times for the same total volume as the single large reactor. The initial cell harvesting step can also be realized with a pressurized filtration system rather than centrifuging, which should greatly reduce the equipment cost. Longevity tests of a 2-h duration also showed photobleaching with concurrent drop in photovoltage. However, these tests showed mixed responses requiring further testing. Work also continued in attempting to coat titanium dioxide nanotubes with bR; however, the surface chemistry that promotes maximal adhesion has not yet been accomplished.

5. References

1. Griep, M.; Cheam, D.; Lueking, D.; Friedrich, C. *Proc. 25th ASC*, 2006.
2. Griep, M.; Winder, E.; Lueking, D.; Friedrich, C. *Proc. SPIE Optics & Photonics* **2007**, 6646, 66460F.

6. Transitions

The following publications and reports have resulted from this work:

1. Karna, S. P.; Mallick, G.; Griep, M. H.; Friedrich, C. R. *Engineered Nano-bio Hybrid Electronic Platform for Solar Energy Harvesting*; ARL-TR-5226; U.S. Army Research Laboratory: Aberdeen Proving Ground, MD, January 2010.
2. Griep, M.; Walczak, K.; Winder, E.; Lueking, D.; Friedrich, C. *Biosensors and Bioelectronics* **2010**, 25, 1493–1497.
3. Walczak, K.; Shokuhfar, T.; Choi, C. K.; Friedrich, C. *Proc. 27th ASC*, 2010.
4. Griep, M.; Winder, E.; Garrett, G.; Karna, S.; Friedrich, C. *Proc. 27th ASC*, 2010 (winner of Best Nanotechnology Paper and winner of the Paul A. Siple Memorial Award for best paper at the 27th Army Science Conference, December 2010).

List of Symbols, Abbreviations, and Acronyms

bR	Bacteriorhodopsin
DSSC	dye-sensitized solar cell
FF	Future Force
KCl	potassium chloride
OD	optical density
PM	purple membrane
PV	photovoltaic
QDs	quantum dots
PSSC	protein sensitized solar cells
SDS-PAGE	sodium dodecyl sulfate polyacrylamide gel electrophoresis
UV	ultraviolet

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